Simultaneous Determination of Fluorine and Chlorine in Rocks by Ion Chromatography in Combination with Alkali Fusion and Cation-Exchange Pretreatment

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Knowledge of the volatile elements behavior in volcanic rocks is of great value for understanding the process of magma generation and differentiation. However, only few studies on volatiles, specifically the halogen content in volcanic rocks, has been made because of the difficulty of the analytical technique. Among the halogens, even though the concentration of fluorine in volcanic rocks is relatively high (<20 - 2000 µg g⁻¹), analytical data on geological reference samples are varied, e.g., 780 – 1163 µg g⁻¹ for JR-1, 81 – 144 µg g⁻¹ for JB-2, 165 – 295 µg g⁻¹ for JA-1.²

Several analytical techniques have been applied to the determination of fluorine in rocks. X-ray fluorescence spectrometry,¹ high-temperature mass spectrometry,⁴ and ion-beam analysis⁶ may be applied directly to solids. The practical difficulties of these techniques are that they require special instruments and/or time-consuming processes. On the other hand, an ion-selective electrode⁵,⁷ gives accurate and precise results, but requires a rather complex preparation stage, e.g., trimethylfluorosilane (TMFS) distillation. Neutron activation analysis⁸ and ICP-MS⁹ have been applied for halogens in rocks, except for fluorine, because of the isotope property or its small ionic radius. The choice of an analytical technique is governed by the reliability and availability of instruments, precision, accuracy, rapidity and simplicity.

In this study, ion chromatography (IC), which is commonly used in many laboratories for sensitive and simultaneous anion determination, was applied to develop a rapid and quantitative method for the determination of fluorine and chlorine in rock samples. This technique requires rendering the samples into a non-acidic solution; for this reason, alkali fusion was done, which is a convenient and practical method for the decomposition of rock samples. After the treatment, however, the sample solution contained great amounts of undesirable anions, which disabled the direct analysis to IC. To eliminate those ions, the sample solution was decarbonated and dehydrated by a cation-exchange treatment. This treatment has been reported for chlorine and bromine determination,¹¹ but not for fluorine, because the dissolved aluminum in the solution from rocks would hinder the fluorine determination.

In this work, aluminum interference on fluorine determination under various pH conditions was investigated in detail; we found the optimal pH condition to minimize the aluminum interference during the cation-exchange pretreatment. Under this pH condition, it was certified that the technique is applicable for chlorine determination as well as fluorine. In the present work, this pretreatment method was applied to the simultaneous determination of F and Cl on six geological reference materials from the Geological Survey of Japan (GSJ), i.e., JR-1, a rhyolite, JA-1 and JA-2, andesites, JB-1a and JB-2, basalts, and JG-1a, granodiorite. The analytical results were compared with published data analyzed by other techniques.

Experimental

Apparatus

Dionex Model QIC (Sunnyvale, Cal, USA) ion chromatographic instrument was used with conductivity detection. Calibration was achieved in the range 0 - 20 ppm of F and Cl by adding known aliquots of NaF and NaCl standard solutions to representative blank solutions.

Reagents

The working standard and spiking solutions were prepared from analytical reagent-grade chemicals using deionized water obtained from a Millipore Milli-Q SP water-purification system.

Recommended procedure

A 0.5-g amount of rock powder was fused with a mixture of 2.0 g Na₂O₂ + 0.5 g Ba(OH)₂·8H₂O in an oven at 500°C for 2 h. The decombustion reagent was carefully prefused to release the water content. The “pancake” was crushed and dissolved in 50 – 60 ml of hot water, followed by filtration. Consequently, the sample solution was passed through a column of 40 ml NH₄⁺-formed cation-exchange resin (SIGMA DOWEX-50W8-200; dry mesh size 100 – 200), collected in a 100 ml volumetric flask, and diluted to the mark with water.

The obtained solution was filtered with a disposal sample preparation cartridge (Advantec 25AS020AN) and injected into the above IC apparatus.

Notes

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the elimination of carbonate and hydroxide. Fluorine showed only 5–11% for a solution of the H⁺-formed 
for the IC column and the majority of Na⁺ are removed. At the 
In the cation-exchange treatment, unfavorable cation elements 
respectively. The possible anions in the post-treatment 
the same time, CO₃⁻, HCO₃⁻ and OH⁻ are removed as CO₂ and H₂O, 
Aluminum forms hydroxide precipitates in the vicinity of pH 7, 
but under higher pH conditions, a large amount OH⁻ would 
Results and Discussion

Solution pretreatment by cation exchange

The solution obtained from alkali fusion is unsuitable for a 
direct analysis by ion chromatography, because the high 
concentration of carbonate and hydroxide in the solution could 
act as an eluent, thus modifying the retention times and causing 
a large analytical peak. The solution should, therefore, be 
pretreated by a cation-exchange resin, both to neutralize the 
solution and to lower the content of the solute (dissolved solids 
in the solution) that may cause IC column overloading. The 
cation-exchange pretreatment is expressed as 
Na₂CO₃ + H⁺-resin → Na⁺-resin + H₂O + CO₂↑.

In the cation-exchange treatment, unfavorable cation elements 
for the IC column and the majority of Na⁺ are removed. At the 
same time, CO₃⁻, HCO₃⁻ and OH⁻ are removed as CO₂ and H₂O, 
respectively. The possible anions in the post-treatment 
solutions are F⁻, Cl⁻, SO₄²⁻ and PO₄³⁻.

After the above pretreatment, however, the determination 
value of fluorine was lower than the expected value. The possible reason of this analytical disagreement was suspected to 
be aluminum interference, which was released from rock 
powders during alkali fusion; it is well known that aluminum 
ion forms a complex and precipitates with F⁻ and OH⁻. Aluminum forms hydroxide precipitates in the vicinity of pH 7, 
but under higher pH conditions, a large amount OH⁻ would 
hinder the formation of aluminum fluoride complex. Therefore, 
to avoid the interferences of aluminum, we sought a pH 
treatment to keep the solution within the desirable pH range, pH > 8, throughout the cation exchange procedure. At the same 
time, the pH condition should be less than ca. 10 to complete 
the elimination of carbonate and hydroxide.

Consequentially, H⁺-formed, NH₄⁺-formed and Na⁺-formed 
resins were investigated concerning aluminum interference 
(Table 1). After this pretreatment, the pH values of the 
solutions were <6, ~8 and >12, respectively. The recoveries of 
fluorine showed only 5–11% for a solution of the H⁺-formed 
resin treatment. A good recovery of 83–97% was obtained for 

Table 1 Influence of aluminum of fluorine determination (the 
pseudotreatment solution contains 5 µg g⁻¹ of fluorine with 1 M of 
NaOH)

<table>
<thead>
<tr>
<th>Fluorine recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>No aluminum</td>
</tr>
<tr>
<td>H⁺-resin</td>
</tr>
<tr>
<td>NH₄⁺-resin</td>
</tr>
<tr>
<td>Na⁺-resin</td>
</tr>
</tbody>
</table>

n: number of determinations. 
n. d.: not detectable for a large OH⁻ peak.

Table 2 Analytical results of the rock samples for JB-2, GSJ 
reference material

<table>
<thead>
<tr>
<th></th>
<th>Fluorine/µg g⁻¹</th>
<th>Chlorine/µg g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>JB-2 H⁺-resin</td>
<td>55±18 (n = 13)</td>
<td>340±32 (n = 10)</td>
</tr>
<tr>
<td>JB-2 NH₄⁺-resin</td>
<td>104±7 (n = 7)</td>
<td>337±44 (n = 4)</td>
</tr>
</tbody>
</table>

n: number of determination.

Spike recoveries

During the analysis, the spike was, however, the determination 
value of fluorine was lower than the expected value. The possible reason of this analytical disagreement was suspected to 
be aluminum interference, which was released from rock 
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ion forms a complex and precipitates with F⁻ and OH⁻. Aluminum forms hydroxide precipitates in the vicinity of pH 7, 
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solutions were <6, ~8 and >12, respectively. The recoveries of 
fluorine showed only 5–11% for a solution of the H⁺-formed 
resin treatment. A good recovery of 83–97% was obtained for 

Table 3 Spike recoveries expressed as the concentration of 
rock samples for JB-1a and JA-1, GSJ reference materials

<table>
<thead>
<tr>
<th></th>
<th>Fluorine/µg g⁻¹</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>JB-1a</td>
<td>38±15 (n = 4)</td>
<td>99</td>
</tr>
<tr>
<td>JB-1a + 400 (µg/g)</td>
<td>780 (n = 1)</td>
<td>99</td>
</tr>
<tr>
<td>JA-1</td>
<td>15±22 (n = 10)</td>
<td>99</td>
</tr>
<tr>
<td>JA-1 + 200 (µg/g)</td>
<td>358±28 (n = 2)</td>
<td>103±4</td>
</tr>
</tbody>
</table>

n: number of determinations.

Table 4 Fluorine and chlorine data (in µg g⁻¹) for GSJ 
reference materials

<table>
<thead>
<tr>
<th></th>
<th>Fluorine</th>
<th>Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference value¹</td>
<td>Present study</td>
<td>Reference value¹</td>
</tr>
<tr>
<td>JR-1</td>
<td>991</td>
<td>106±157</td>
</tr>
<tr>
<td>JB-1a</td>
<td>357</td>
<td>38±115</td>
</tr>
<tr>
<td>JB-2</td>
<td>98±3</td>
<td>104±7</td>
</tr>
<tr>
<td>JA-1</td>
<td>161</td>
<td>153±22</td>
</tr>
<tr>
<td>JA-2</td>
<td>227±20</td>
<td>227±20</td>
</tr>
<tr>
<td>JB-1a²</td>
<td>439</td>
<td>43±450</td>
</tr>
</tbody>
</table>

a. The sample powder of JG-1a was prefused with ZnO in addition to 
Na₂O₂ + Ba(OH)₂·8H₂O to lower the melting point. The Cl data on 
JG-1a were widely scattered due to presence of an impurity of Cl in 
ZnO.

b. Not determined.

Analysis of reference materials

The analytical results obtained from this work and the 
published values for reference materials are summarized in 
Table 4. A good agreement for fluorine and chlorine has been 
obtained between the results of this present work and the 
recommended values by Geological Survey of Japan (GSJ).¹² 
This signifies that the recommended cation exchange procedure 
used in this study is reasonably accurate and precise.
Conclusion

The feasibility of using IC for the simultaneous determination of fluorine and chlorine in rock samples, following the cation exchange of the sample solution, was successfully demonstrated. The results demonstrate that this technique is highly reproducible, and agree well with the results of other analytical techniques.

Acknowledgements

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References